Method for Measuring Water Diffusion in a Coating Applied to a Substrate

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INTRODUCTION

Water at the interface is often the main cause of corrosion, blistering, and disbondment of organic coating/substrate systems. Consequently, the transport of water from the environment to the coating/substrate interface is the subject of great interest in many industries such as organic coatings, asphalt pavements, and electronic packaging. There is no suitable method available to measure the transport of water in an organic coating applied to a substrate (applied film). The majority of information available in the literature on the transport of water in organic coatings is from studies of free (detached) films.[1-3] However, the characteristics of water migration through a free film and an applied film may not be the same. For example, Holtzman[4] observed that water permeabilities of applied films were slightly lower than those of free films. Results of a sorption study by Rosen and Martin[5] also showed the same trend for the diffusion coefficient of water in alkyd coatings. However, they found the diffusion coefficients of water in epoxy coatings applied to steel substrates were almost three times greater than those in the free films. Discrepancies in the transport of water between free and applied films were also found in studies of water uptake in organic coatings. Several workers[6-9] reported appreciably higher water uptake in applied films than in free films while others[10,11] found the reverse; that is, the amount of water sorbed in the applied films was less than that in the free films. These results raise serious doubts about the extrapolation of data from the transport of water in free films to the applied films used in actual practice.

The two techniques that have been used to provide information on water transport in coatings applied to a substrate, namely, capacitance[4] and gravimetry,[5] are based on the amount of water taken up by a coating attached to a substrate. Due to the reactivity of the coating/metallic interface and the oxides on the substrate surface, water diffusivity cannot always be deduced from the capacitance data.[12] However, the main drawback of both the gravimetric and capacitance techniques is that they do not discern the water accumulated at the coating/substrate interface from that sorbed in the bulk of the coatings. If water is adsorbed at the coating/substrate interface, these methods would incorrectly estimate the rate of water transport in a coating applied to a substrate.

The accumulation of water at the coating/substrate interface is inevitable when an organic-coated specimen is exposed to water or high relative humidities. This is because the bonds

A method based on Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy was developed for measuring the apparent diffusion coefficient of water in a coating applied to a substrate. The method requires an application of a coating of any thickness on an internal reflection element, which serves as the substrate, with the attachment of a water chamber to the coated specimen. Water is introduced to the chamber and FTIR-MIR spectra are collected automatically without disturbing the specimen or the instrument. The amount of water at the coating/substrate interface was determined using a model based on the theory of internal reflection spectroscopy. A mass-time curve for water at the interface is established, which provides the time-lag value, the time required for water to diffuse through the coating film and reach the interface. The diffusion coefficient (D) is then determined by the time-lag equation. For thick coating films (> 25 µm), D may be estimated from the FTIR-MIR in situ intensity data only. The sensitivity of FTIR-MIR spectroscopy and the strong FTIR absorption of water molecules make this an ideal method for measuring the diffusivity of liquid water through a coating applied to a substrate.

between an organic coating and a high surface-free energy (>100 mJ/m^2), inorganic or metal (oxide) substrates are generally not thermodynamically stable in the presence of aqueous solutions.[13-16] Consequently, water molecules are likely to break these bonds and layers of water are adsorbed at the coating/substrate interface when an organic-coated, high-energy substrate is exposed to a humid environment. Leidheiser and Funke,[17] in a critical review on water disbondment of coated metals, believe that a water film many molecular layers

thick at the coating/metal interface is the main reason for the disbondment of organic coatings on metals. Similarly, in an intensive study on the mechanism of the sudden loss of adhesion in high water activity, Lefebre et al.[18] postulated that above the threshold humidity, water "condenses" on the hydroxyl groups of the polymer, causing rupture of the interchain hydrogen bonds and displacement of the adsorbed hydroxyl groups from the surface of the substrate. Evidence for the presence of water at the coating/substrate interface also comes from the work of Funke and Haagen,[7] who observed a "crossover" in the water uptake curves for the applied and free films. They attributed the higher uptake in the applied film to the accumulation of water at the coating/substrate interface. Other evidence is from spectroscopic studies by Nguyen et al.,[19,20] who showed that, depending on the coating/substrate system, the water layer at a coating/inorganic substrate interface can be tens of monolayers thick. By the use of a neutron reflectivity technique, Wu et. al.[21] also reported a water layer of about 3 nm thickness at the interface between a polyimide and a single crystal silicon wafer.

The amount of water at the coating/substrate interface is increased if there exists a driving osmotic force between the interface and the external environment[17,22] or the presence of hydrophilic materials at the interface. One example for the latter case is from a study by Walker,[23] who found that the degree of adhesion loss of a coating on a metal substrate exposed to water is related to the water-sensitive layer formed at the coating/metal interface. Another example is inferred from the results of Bowden and Throssell,[24] which showed that, even at a relative humidity of 50%, a metal surface contaminated with $10^{-7} g/cm^2$ of potassium hydroxide sorbs the equivalent of five molecular layers of water. Unfortunately, water-soluble inorganic and organic salts are almost ubiquitous contaminants at the organic coatings/high energy substrate interface, being either present before the film application or built-up during exposure. These examples strongly indicate that the accumulation of water at the organic coating/substrate interface is unavoidable during exposure to an aqueous environment. Thus, there is a need for a method to determine the rate of water transport through a coating applied to a substrate that accounts for water at the coating/substrate interface. This study describes such a method based on the use of Fourier transform infrared spectroscopy in the multiple internal reflection mode to measure the amount of water built-up at the coating/substrate interface as a function of time. The data are then used to determine the apparent diffusion coefficient of water in an organic coating applied to a substrate using the time-lag approach.

BACKGROUND

Water Diffusion in Coatings

From the instant water is admitted to the coating side of the coated substrate and prior to the attainment of a steady flow, both the rate of flow and the concentration of water at any point within the coating layer vary with time. If the diffusion coefficient is constant and the initial concentrations of water within the coating film and at the coating/substrate interface are negligible, the amount of water which passes through the coating layer in time t is given by the non-steady state equation:[25]

$$\frac{Q_w}{l_c C_1} = \frac{Dt}{l_c^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp(\frac{-Dn^2\pi^2 t}{l_c^2}) \qquad (1)$$

where Q_w is the total mass of water passing by diffusion through the organic film in time t, l_c is the thickness of the coating, C_1 is the concentration of water on the outside surface of the coated substrate, D is the apparent diffusion coefficient, and n is an integer. The mass-time plot of equation (1) has an initial build-up period but a linear relationship develops as t→∞. For the derivation presented in this study, we are interested only in the finite interval of time before steady state is achieved. Under these conditions, equation (1) simplifies to[25]

$$Q_w = \frac{DC_1}{l_c} (t - \frac{l_c^2}{6D}) \qquad (2)$$

and the mass-time plot has an intercept, t_{in}, on the t-axis (horizontal) given by

$$t_{in} = \frac{l_c^2}{6D} \qquad (3)$$

where t_{in} is known as the "time lag." t_{in} is the time required for water to diffuse through the coating and reach the coating/substrate interface. Equation (3) provides the basis for the determination of D by the time-lag approach. It is noted that in the absence of heterogeneity and time effects, there should be no difference between D values obtained by the time-lag method and those derived from the steady-state approach if Fick's equations are valid.[26]

Based on the time-lag approach, the diffusion coefficient of water in a free film can be obtained by determining the amount of water exiting the other side of the film. For a coating applied to a substrate, the diffusion coefficient may be derived by measuring the amount of water accumulated at the coating/substrate interface over a finite time interval. This can be accomplished by using Fourier transform infrared-multiple internal reflection spectroscopy (FTIR-MIR) in situ measurement of coated specimens exposed to water.

Fourier Transform Infrared-Multiple Internal Reflection Spectroscopy

Fourier transform infrared spectroscopy (FTIR) has been recognized as a powerful technique to provide quantitative information on complex molecules. Since the intensity recorded by FTIR spectroscopy is proportional to the concentration of the material, this technique can be used for studying the diffusion of materials in coatings. One of the FTIR techniques, which provides quantitative information in situ, is FTIR-MIR or FTIR-ATR (attenuated total reflection). In this technique, the evanescent field, produced on total internal reflection in the substrate, interacts with the material of interest and causes an attenuation of the reflection of the propagating beam. Detection of the attenuated radiation at the exit of the substrate yields an infrared spectrum of the sample. This unique mode of interaction has made possible a large number of applications, with new applications being developed each year. These applications take advantage of the technique's ability to probe the near surface layers of solids and liquids. The use of this technique for measuring the diffusion coefficients of water, carbohydrate, polymers, and solvent in polymers has been demonstrated recently.[27-30] Pre-

viously, we have employed this technique for detecting and quantifying water *in situ* at the organic coating/substrate interface.[19,20,31,32] Since this technique provides quantitative data on the water layer at the interface after the water has migrated through the thickness of the coating films, it should provide a unique way for measuring the apparent diffusion coefficient of water in an organic coating applied to a substrate.

The theoretical basis of the method for determining the amount of water at the coating/substrate interface is derived from the penetration-depth concept of internal reflection spectroscopy developed by Harrick[33,34] for thin and thick films. The validity of this concept for quantitative studies of polymeric systems has been demonstrated.[35-38] A detailed description of the model in which water at the coating/substrate interface is quantified by the FTIR-MIR technique is given in reference 19. The following section provides pertinent information for aiding in the study of the diffusion of water in a coating applied to a substrate.

The absorbance, A, of a band in an IR internal reflection spectrum of a surface film having a thickness, L, on a substrate is given by[33]:

$$A = \frac{n_2 \, \alpha \, E_o^2}{n_1 \cos\theta} \int_0^L e^{(\frac{-2z}{d_p})} \, dz \tag{4}$$

where α is the absorption coefficient per unit thickness for the band of interest, θ is the incident angle, n_2 and n_1 are the refractive indices of the sample and substrate, respectively, z is the depth from the interface, E_o is the amplitude of the evanescent wave at the surface, and d_p is the depth at which the amplitude of the evanescent field has decreased to 1/e of its value at the surface. d_p is commonly defined as the penetration depth of the evanescent wave, which is given by[34]:

$$d_p = \frac{\gamma}{2 \, \pi \, n_1 \, [\sin^2\theta - (\frac{n_2}{n_1})^2]^{\frac{1}{2}}} \tag{5}$$

where γ is the wavelength of the infrared radiation in vacuum. More than 85% of the total absorption intensity of a band is within one d_p,[37,38] whereas the probing depth of internal reflection spectroscopy is limited to three times d_p.[36] Equation (5) explicitly indicates that the penetration depth of the evanescent wave in the sample is a function of the angle of incidence, the wavelength of the radiation, and the refractive indices of the substrate and the sample. Equation (5) is generally valid for nonabsorbing or weakly absorbing materials. For absorbing functional groups, Muller et al.[39] have derived a more exact equation for d_p, which uses the complex refractive index $n_2/n_1(1 + i\kappa)$ (κ is the extinction coefficient) in place of the simple refractive index n_2/n_1. Further, due to the rapid change in the magnitude of n_2 around the center of an absorption band (dispersion effect), d_p in the vicinity of the peak maximum may be different from that at or away from it, particularly for low n_1 and low θ,[34] as demonstrated recently by simulation.[40] However, Nguyen et al.[19] have shown that the effect of absorption on d_p is negligible at the OH stretchings (3400cm⁻¹) of water and epoxy and that, at this frequency, equation (5) is valid for computing d_p in these materials.

When an organic-coated specimen is exposed to an aqueous environment, water will enter the coating/substrate interfacial region and interact with the evanescent wave and be detected. The total amount of water detected is the sum of the amount of the water layer at the coating/substrate interface

and that of water taken up in the coating layer probed by the evanescent wave.[31] Using infrared absorbance to express the amounts of water, this statement may be written as[19]:

$$A(t) = \frac{n_2\alpha_2 E_o^2}{n_1 \cos\theta} \int_0^{l_w} e^{(\frac{-2z}{d_{pw}})} \, dz + \frac{c_{w(t)}n_3\alpha_3 E_o^2}{n_1 \cos\theta} e^{(\frac{-2l_w(t)}{d_{pw}})} \int_{l_w}^{\infty} e^{(\frac{-2z}{d_{pc}})} \, dz \tag{6}$$

where $A(t)$ is the FTIR-MIR absorbance of the water band, n_2 and α_2 in this case are the refractive index and absorption coefficient of water at the coating/substrate interface, n_3 and α_3 are the refractive index and absorption coefficient of sorbed water in the coatings, $l_w(t)$ is the thickness of the water layer at the coating/substrate interface, d_{pw} and d_{pc} are the penetration depths of the evanescent wave in water and coating, respectively, and $c_w(t)$ is the mass fraction of water sorbed in the coating. $A(t)$, $l_w(t)$, and $c_w(t)$ vary with time of exposure. The first term of equation (6) is the absorbance (FTIR) corresponding to the amount of water at the coating/substrate interface and the second term represents the amount of water in the coatings within the probing depth of the evanescent wave.

Assuming that the refractive index and absorption coefficient of water at the coating/substrate interface are the same as those for water sorbed in the coating, i.e., $n_2 = n_3$ and $\alpha_2 = \alpha_3$ (a reasonable assumption), integrating and rearranging equation (6) yields an expression for calculating the thickness of the water layer at the coating/substrate interface as a function of time $l_w(t)$:

$$l_w(t) = \frac{d_{pw}}{2}[-\ln\frac{1 - \frac{A(t)}{A_\infty}}{1 - c_w(t)\frac{d_{pc}}{d_{pw}}}] \tag{7}$$

where

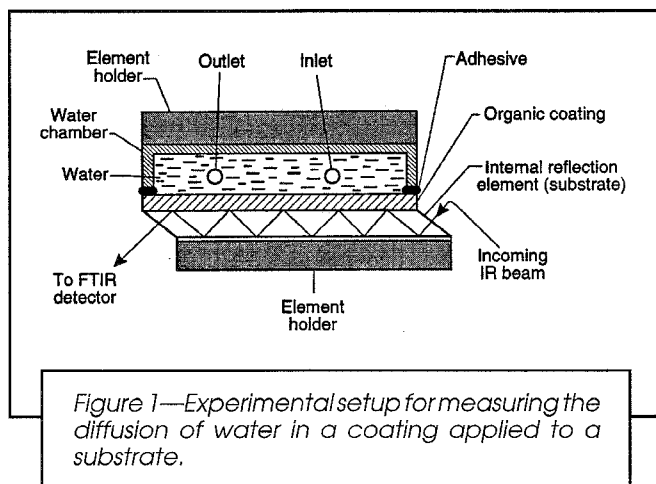$$A_\infty = \frac{n_2 \, \alpha_2 \, E_o^2 \, d_{pw}}{2 \, n_1 \, \cos\theta} \tag{8}$$

A_∞ is the infrared absorbance when the water layer at the coating/substrate interface is very thick ($l_w(t)\to\infty$, i.e. $l_w(t)>d_{pw}$). Physically, this means that the water layer at the interface is so thick that the amplitude of the evanescent wave decays to a negligible value within it. In this instance, only the first term of equation (6) remains. Equation (7) is still valid for the case where the water layer at the coating/substrate interface is not continuous, e.g., discrete droplets, provided that the height of the droplet is not greater than the probing depth of the evanescent wave in water. Reference 19 gives a detailed derivation of equation (7) from equation (6).

Assuming water is uniformly distributed over the entire surface area of the spectrum, the amount of water at the coating/substrate interface, $Q_{wi}(t)$ will be given by:

$$Q_{wi}(t) = l_w(t) \, a \, \rho \tag{9}$$

where a is the area in contact with water and ρ is the density of water at the interface.

To obtain $Q_{wi}(t)$, data on $A(t)$, A_∞, $c_w(t)$, d_{pc}, and d_{pw} in equation (7) must be known. $A(t)$, the absorbance corresponding to the total amount of water detected at a given exposure time, is derived from the FTIR-MIR *in situ* measurement of coated specimens exposed to water; A_∞, the FTIR-MIR absorbance of water of indefinite thickness, is deter-

Figure 1—Experimental setup for measuring the diffusion of water in a coating applied to a substrate.

mined from the FTIR-MIR spectrum of water in contact with the coating-free substrate; $c_w(t)$, the mass fraction of water sorbed in the coating within the probing depth at a given time, is extrapolated from the water uptake in free films; and d_{pc} and d_{pw} are calculated from equation (5).

In short, the method described in this paper for measuring the diffusion of water in a coating applied to a substrate requires two main tasks: (1) conducting experiments to provide $A(t)$, A_∞, $c_w(t)$ data to determine $Q_{wi}(t)$; and (2) plotting $Q_{wi}(t)$ versus exposure time to obtain the time lag, t_{in}, which yields D via equation (3). In this paper, the apparent diffusion coefficients of three organic coatings on three substrates are determined to demonstrate the method.

EXPERIMENTAL

Three separate experiments were carried out: (1) FTIR-MIR *in situ* measurement of organic-coated specimens exposed to water; (2) FTIR-MIR analysis of water in contact with the coating-free substrates; and (3) water uptake in the free films. All experiments were performed at ambient temperature (22°C). These experiments will provide data for $A(t)$, A_∞, and $c_w(t)$, respectively.

FTIR-MIR IN SITU MEASUREMENT OF COATED SPECIMENS EXPOSED TO WATER: Specimens of one alkyd and two epoxy coatings applied to three substrates were used. The alkyd coating was a pigmented, solvent-based topcoat. It contained, by mass, 31.5% TiO$_2$ and 16% reinforcing pigments, and 26.5% mineral spirit as the solvent. The epoxies were a pigmented, water-reducible and a pigmented powder coating. The water-reducible epoxy coating was a stoichiometric mixture of a water-reducible epoxy resin and an amine adduct, used as the curing agent. The resin is 53% solids; the solvent was a mixture, by volume, of 83% water and 17% 2-propoxyethanol. The curing agent contained 40% solvent, comprised of 95.5% 2-propoxyethanol and 4.5% glacial acetic acid. The chemical structures of the resin and curing agent were unknown. The water-reducible epoxy coating had 15% TiO$_2$ pigment. The powder epoxy, which contained 2% inorganic pigment, was a commercial, fusion-bonded product used for pipeline applications. Scanning electron microscopy analysis revealed that the cured powder epoxy films contained numerous air voids having diameters ranging from 10 to 100 μm.

The three substrates were 50 x 10 x 3 mm spectroscopic grade, 45° parallelogram internal reflection elements (IRE) of germanium (Ge), silicon (Si), and thallium bromide iodide (KRS-5). At a 45° incident angle, these elements provide 17 reflections inside the substrates. When received, each IRE (substrate) was wrapped in a soft cloth and hermetically sealed in a plastic envelope inside a rigid box containing desiccant and packaging foam. Except for KRS-5, the substrates were employed as received immediately after unwrapping without surface cleaning or treatment. The KRS-5 substrate was a repolished IRE, which has been in use. Although this IRE has lost some infrared throughput, it was found sufficient for this experiment. The Si IRE surfaces had a 2.25 nm SiO$_2$ layer (as measured by an ellipsometer), which was covered with silanol (SiOH) groups and adsorbed water.[32] Thus, the chemical functional groups on the surfaces of this substrate are similar to those of industrial metals such as steel and aluminum, which are, under normal conditions, covered with hydroxylated oxide.[41] The SiO$_2$-covered Si IRE is designated as the SiO$_2$-Si substrate. Although the surfaces of the other two substrates were not characterized, they were also probably covered with adsorbed water before applying the coating because these substrates and their oxides are highly energetic. The alkyd was applied on the SiO$_2$-Si, the water-reducible epoxy on the Ge, and the powder epoxy on the KRS-5 substrate.

The coating application procedure used for the alkyd and water-reducible epoxy was similar to that described previously for other coatings.[19,31] Briefly, except for the surface to be coated, all sides of the 50 x 10 x 3 mm substrate were covered with masking tape. The coating was applied by flooding on one end of the substrate then firmly pulled down toward the other end using a round glass rod. Adhesive tape strips of 1 mm wide placed along the length of the substrate were used to control the thickness of the coatings. Four hours after a coating was applied, the 1-mm adhesive tape strips were removed. The bare areas (where the tape strips were removed) were covered with the same coating (by brushing). It should be mentioned that the coating layer around the edges (where the walls of the water chamber are attached) was made (by brushing) substantially thicker than the rest of the specimen. This was to insure that the only pathway for migration of water from the outside to the interface was through the thickness of the coating within the walls of the water chamber.

The application of powder epoxy on the KRS-5 substrate was carried out on a customized line in a plant used for coating reinforced steel bars. Before applying the coating, except for the face to be covered with the powder, all sides of the KRS-5 substrates were masked with a pressure-sensitive adhesive tape. The substrates were then mounted on a steel panel using adhesive tape. The steel panels with the mounted KRS-5 substrates were then hung on the conveyor, which traveled at a speed of 2.4 meters per minute. Immediately after preheating at 215°C for 11 min in a 27-m length oven, the substrate was coated manually with the powder using an electrostatic gun. It should be noted that the entire unmasked surface of the KRS-5 substrate was covered with powder coating and that the coating thickness of this specimen was controlled by the manner in which the coating was sprayed. The coated substrate was then cured at 204°C for 11 min. The quality of the coated specimens of all three coatings was good and no visible pinholes or air bubbles were observed (by the naked

eye) on the specimen surfaces. The coating thicknesses of all specimens were measured, using a micrometer, on the dried, free films removed from the substrates after the conclusion of the experiment. The thickness of each coating was reported as the average of four measurements.

Figure 1 illustrates the experimental setup used for measuring the diffusion of water in a coating applied to a substrate. After curing, a water chamber was attached to each coated specimen. The chamber had the same length and width as those of the substrates, i.e., 50 x 10 mm and a wall thickness of 1.5 mm. This gives an area of the coating in contact with water of 329 mm². Each chamber was closed on five sides, leaving open the side to be attached to the coated substrate. One side of the chamber contained inlet and outlet ports to introduce and remove water. In situ measurements of specimens exposed to water were carried out using an FTIR spectrometer with a variable angle ATR accessory. The spectrometer was equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. The specimen with the water chamber attached was placed vertically in an ATR accessory holder. It is noted that, prior to putting the specimen in the holder, all masking tapes were removed and all uncoated surfaces of the substrates were cleaned by wiping repeatedly with a piece of cotton soaked with methylene chloride solvent. After inserting the ATR accessory with the mounted specimen in the spectrometer, and prior to filling the chamber with water, FTIR-MIR spectra of the unexposed specimens were taken. Distilled water was then added to the chamber and the inlet and outlet ports were sealed to prevent water evaporation. FTIR-MIR spectra of the water-exposed specimens were taken automatically at specified intervals (one hour for the alkyd and every 15 min for the two epoxies) until the experiment was complete. There was no disturbance to the spectrometer or to the specimens throughout the measurements. The spectrum obtained was the ratio between the single beam spectrum taken at each exposure time and that of the background (specimen-free spectrometer). Difference spectra were acquired by subtracting the spectrum of the unexposed specimen from that of the water-exposed specimen. All spectra were taken at a 4 cm⁻¹ resolution using 32 scans and purged dry air. Unpolarized radiation at an angle of incidence of 45° was used. The "peak height" method, which measures the absorbance at the absorption maximum of the band of interest, was used for quantitative analyses.

FTIR-MIR ANALYSIS OF WATER ON COATING-FREE SUBSTRATES: In this study, a water chamber was attached to the coating-free substrates using a silicone adhesive. After filling the chamber with distilled water, FTIR-MIR spectra of water were collected using the same procedure described for the in situ measurement, except that there was no organic coating film on the substrates. The

spectrum of water was the ratio between the single beam spectrum of water in contact with the coating-free substrate and that of the water-free, coating-free substrate with the chamber attached.

WATER UPTAKE IN FREE FILMS: The water uptake in free films was measured using the gravimetric method. Free films of alkyd and water-reducible epoxy coatings were obtained by applying the coatings on a thick aluminum foil and a glass substrate, respectively, using the drawdown technique. Both substrates were used without surface treatment. The free films of the powder epoxy coating were procured by applying the powder on matte-finish steel panels that had been treated with a fluoropolymer release agent. Before applying the powder coating, the fluoropolymer treated panels were baked in an oven at 200°C for four hours to maximize the solvent removal and to ensure a good film formation of the release agent on the substrate. The effect of the fluoropolymer release agent on the water uptake of the powder epoxy is expected to be minimal, because water was sorbed from both sides of the free films. The release-agent treated panels were hung on the conveyor, preheated, coated with the powder, and cured at the same time with the KRS-5 substrate. Cured films of all three coatings were peeled off readily from the substrates. Free films were cut to size, weighed, and immersed in distilled water. They were taken out, blotted, and reweighed at specified time intervals. The thickness of each free film specimen was measured at three locations using a micrometer. The thickness of the alkyd, water-reducible epoxy, and powder epoxy free films were 109, 96, and 155 μm, respectively. Water uptake was expressed as a fraction of the mass of the initial, dry specimen. The results from three specimens of each coating were averaged.

RESULTS AND DISCUSSION

Amount of Water at the Coating/Substrate Interface

The amount of water at the applied film/substrate interface was determined using equations (7) and (9) and the results

Figure 2—Typical FTIR-MIR spectra in the 2800-3800 and 1400-1800 cm⁻¹ regions of a 140 μm thick organic coating applied to a substrate exposed to liquid water for different times.
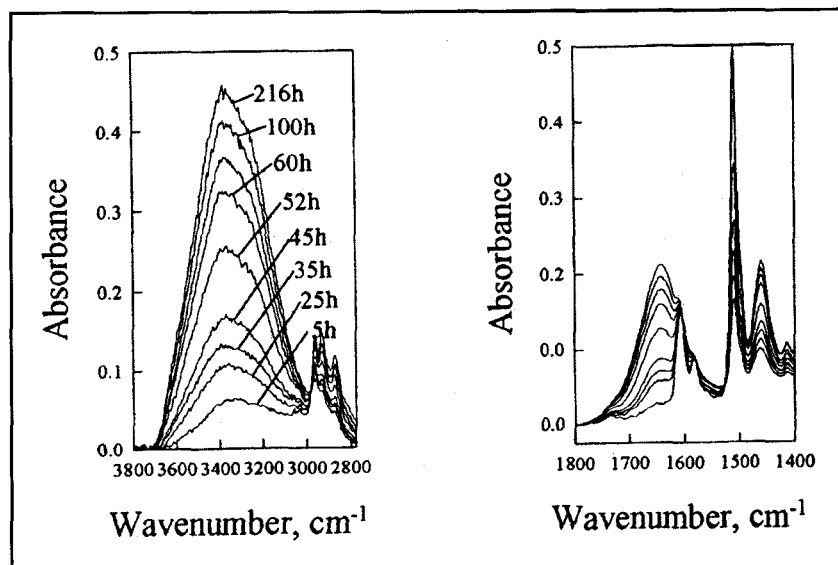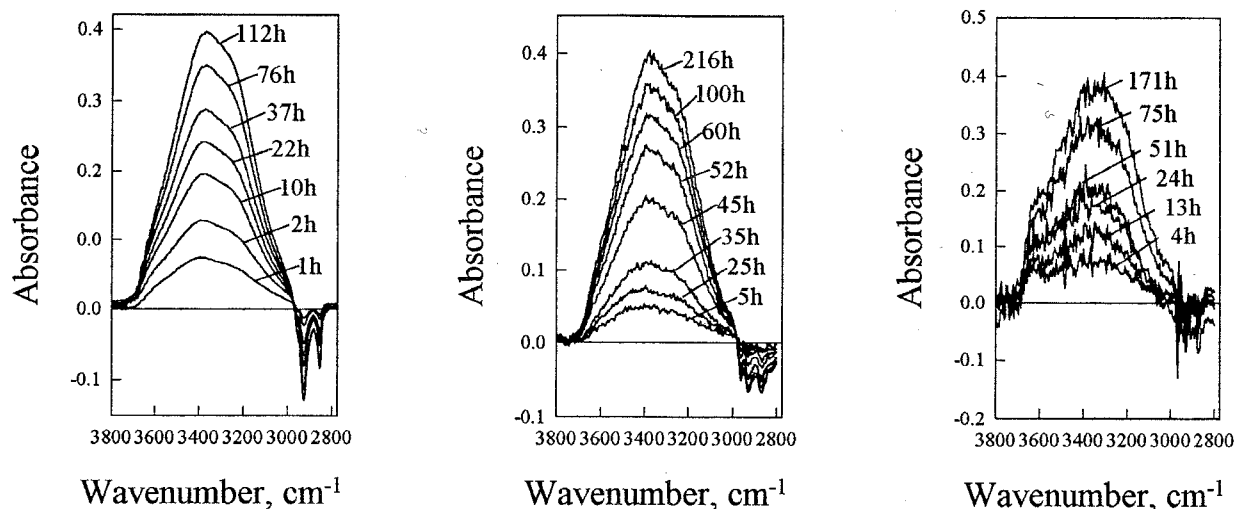
Figure 3—FTIR-MIR difference spectra in the 2800-3800 cm^{-1} region of three organic-coated specimens exposed to liquid water for different times: (1) alkyd/SiO$_2$-Si; (b) water-reducible epoxy/Ge; and (c) powder epoxy/KRS-5.

provided by the three experiments previously described. Data on the absorbance (FTIR) at a given exposure time in water, A(t), were obtained from the spectra of the FTIR-MIR *in situ* experiments of coated specimens exposed to water. Typical results are displayed in *Figure* 2, which shows FTIR-MIR spectra in the 2800-3800 and 1400-1800 cm^{-1} regions (regions of water OH stretching and bending, respectively) for an epoxy coating on a substrate taken before and during exposure to water for different time intervals. Each spectrum was obtained by ratioing the spectrum of the exposed specimen against the corresponding background spectrum, as described in the Experimental Section.

Although the effects of water are evident in the 3000-3650 and 1625-1750 cm^{-1} regions, these spectra still contain the
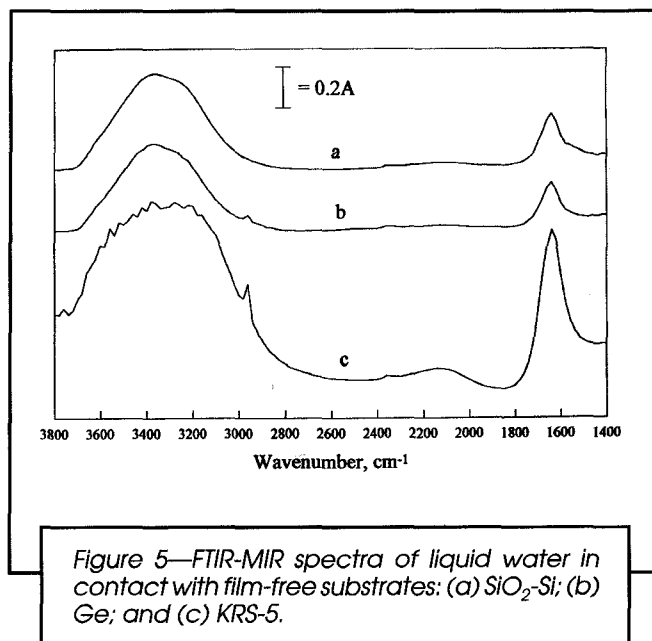

Figure 4—Intensity changes of the water OH stretching band as a function of exposure time: (a) alkyd/SiO$_2$-Si; (b) water-reducible epoxy/ Ge; and (c) powder epoxy/KRS-5. (Each dot represents a data point).

absorbance bands of the coatings. To provide quantitative information on the water layer at the coating/substrate interface, the FTIR-MIR absorbance from the coatings must be nullified. This was done by subtracting the spectra collected before exposure to water from those acquired at different exposure times. *Figure* 3 presents these spectra (difference spectra) for three coatings on three substrates in the 2800-3800 cm^{-1} region. The relatively high "noise" in the spectra of the powder epoxy/KRS-5 specimen was probably due to the poor quality of the KRS-5 IRE, as stated earlier. However, the poor quality of these spectra did not affect the ability to detect intensity change in the 3000-3650 cm^{-1} region, which is the main region of interest. The thicknesses of the alkyd, water-reducible epoxy, and powder epoxy coatings were 143 ± 7, 140 ± 9, and 240 ± 10 µm, respectively. As emphasized earlier, there were no mirror or sample adjustments throughout the measurements. If there were no effects due to water exposure, all difference spectra would be straight lines, with the exception of the intensity fluctuations of the CO$_2$ bands from the air in the spectrometer. Bands above or below the baseline of a difference spectrum indicate an increase or a decrease, respectively, of the concentration of a chemical functional group as a result of water exposure.

Difference spectra (*Figure* 3) clearly demonstrate the effects of water on the organic-coated specimens. The intensity of the bands in the 3000-3650 cm^{-1} region increased, while the intensity of the coating bands, e.g., at 2850 cm^{-1}, decreased with time of exposure to water. These changes are the result of water entering the coating/substrate interfacial region and interacting with the evanescent wave. The band near 3400 cm^{-1} is due to the OH stretching mode of molecular water, as verified previously for coatings on Ge and SiO$_2$-Si substrates.[19,31] The intensity, expressed as peak height, of the 3400 cm^{-1} band was chosen for the quantitative analysis of water at the coating/substrate interface. The bending mode of water at 1640 cm^{-1} was found to be insensitive to water at low concentrations,[32] and thus was not used for the analysis. *Figure* 4 depicts the intensity change of the 3400 cm^{-1} band as a
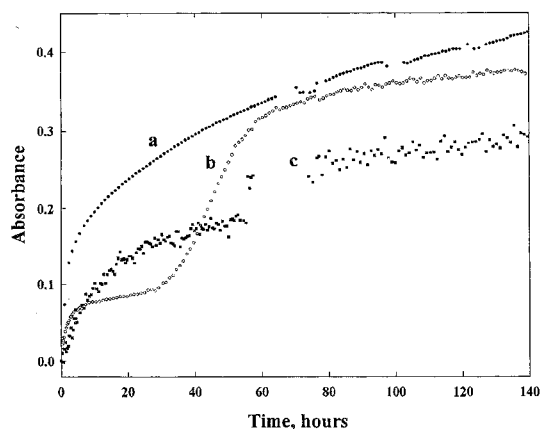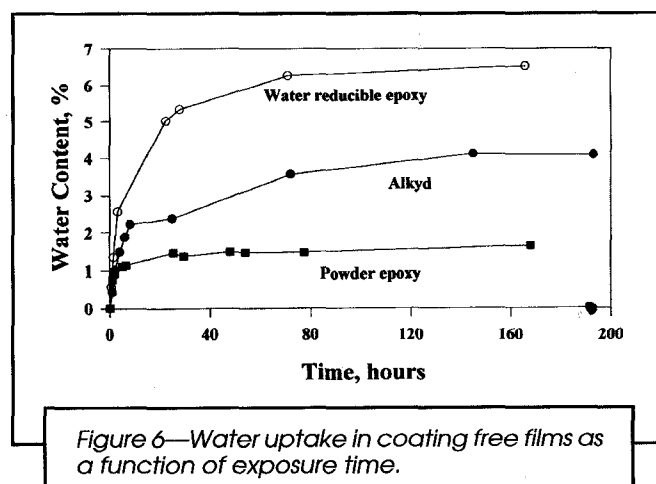
function of exposure time for the three specimens. (Note that data points between 60 and 75 hr exposure for curve c are missing due to a power outage.) The concentration of detected water increased rapidly at short exposure times; thereafter, it rose at a slower rate. It is noted that the absorbance intensity at each exposure time displayed in *Figure* 4 represents the total amount of water detected. This water is comprised of the water at the coating/substrate interface and water in the coating film within the probing depth of the evanescent wave, as stated earlier. The intensity at each exposure time taken from each curve of *Figure* 4 provides an $A(t)$ value in equation (7).

The FTIR-MIR absorbance of water on the coating-free substrate, A_∞, was measured from the experiments of FTIR-MIR analysis of water in contact with film-free substrates. The results are presented in *Figure* 5, which shows FTIR-MIR spectra of double distilled water on SiO_2-Si, Ge, and KRS-5 substrates. These are considered spectra of bulk water because the probing depths of the evanescent wave in the samples are several hundred nanometers. *Figure* 5 shows little difference in band shapes of liquid water on SiO_2-Si and Ge substrates. On the other hand, the spectrum of water on the KRS-5 substrate exhibits a much broader peak in the 3000-3650 cm^{-1} region than those on the other two substrates. There is also a difference in intensity in both the 3000-3650 and 1625-1645 cm^{-1} regions among the three spectra. The difference is mainly due to the difference in the refractive indices between the three substrate materials, which produces a difference in their d_p values in water. All three FTIR-MIR spectra of liquid water on three different substrates exhibit a broad band peaking near 3400 cm^{-1}, due to hydrogen-bonded OH stretching, and a band near 1640 cm^{-1}, due to H–O–H bending. These results again confirm the band at 3400 cm^{-1} in *Figure* 3 as due to water entering the coating/substrate interfacial region. The value of A_∞ in equation (7) is taken directly from total absorbance at the 3400 cm^{-1} position of each spectrum in *Figure* 5.

The amount of water sorbed in the bulk coating within the probing depth of the evanescent wave, c_w, was determined from the water uptake in the free films; these results for three coatings are given in *Figure* 6. The maximum water uptakes in the alkyd, water-reducible epoxy, and powder epoxy free films were approximately 4.1, 6.6, and 1.5%, respectively. The mass fraction of water sorbed in the coatings within the evanescent probing depth at a given exposure time [$c_w(t)$ in equation (7)] was linearly interpolated from the results of *Figure* 6 after multiplying the time scale (horizontal axis) by two. Time scale doubling was used to provide a rough correction for the difference between the water sorption process in the FTIR-MIR measurement (*Figure* 1) and that in the water uptake in coating free films. Water sorption in the former was from one face of the coating while that in the latter took place on both faces of the films. The interpolation was made assuming that water was uniformly distributed in the coatings and that water entered the interface as soon as it reached there. The arguments to support these assumptions have been given elsewhere.[19] We also made the analysis of water at the coating/substrate interface for the case where water was allowed to saturate the coatings (maximum water uptake in the coating) before reaching the interface.[32] The results showed essentially no difference in the amounts of water at the interface between the two cases (c_w as a function of exposure time versus c_w at maximum uptake).

Figure 5—FTIR-MIR spectra of liquid water in contact with film-free substrates: (a) SiO_2-Si; (b) Ge; and (c) KRS-5.

Determination of the amount of water at the coating/substrate interface using equation (7) also requires information on the penetration depths of the evanescent wave in the coating films, d_{pc}, and in water, d_{pw}, at the wavelength of interest. For water and polymer coatings, these values at the OH stretching frequency were computed from equation (5) using an angle of incidence of 45°, and refractive index values as follows: Ge = 4, Si = 3.5 and KRS-5 = 2.4,[34] water = 1.30,[42] and coating = 1.5.[43] Although the refractive index of a pigmented coating is a composite of the polymer and the pigment,[44] we used a refractive index value of an unpigmented polymer for the calculation. The rationale for this use, as well as the omission of the thin SiO_2 layer on the Si IRE in the calculations of d_p, were presented earlier.[19] At the water OH stretching band (3400 cm^{-1}, 2.94 μm), d_p values in the polymer films on Si, Ge, and KRS-5 substrates were 0.24, 0.20, and 0.59 μm, respectively, and in water were 0.22, 0.19, and 0.43 μm, respectively. Since the majority (>85%) of the intensity of a band is from this depth, these results indicate that most of the water molecules detected were from those close to the coating/substrate interface (<1.0 μm).

Figure 6—Water uptake in coating free films as a function of exposure time.

0% relative humidity).[1] For pigmented coatings, D values obtained by the wet cup test were higher than those given by the dry cup test. However, there was essentially no difference in D values determined by the two tests for clear coatings.

The diffusion coefficients for liquid water measured by the method presented in this paper were for coatings applied to a substrate. These values may be influenced by the effects of, e.g., inhomogeneities, defects, water-soluble species, and internal stresses in the coatings, as well as the effects of coating/substrate interfacial properties. The rate of water transport through a coating applied to a substrate is controlled by the osmotic pressure gradient as was demonstrated by Kittleberger and Elm[22] and van der Meer-Lerk and Heertjes[46] many years ago. The implication of these studies is that the presence of hydrophilic contaminants at the coating/metal interface should have a great influence on the diffusion of water through organic coatings applied to a substrate. Thus, the diffusion coefficients determined by the method described here better represent the transport of liquid water through coated films in actual practice than do the values obtained for liquid water transport through free films.

In the procedure previously described, the amount of water at the coating/substrate interface was determined (*Figure* 7) for calculating D. However, for thick coating films (>25 μm), only change of the water band intensity with time (*Figure* 4) is needed to estimate a value for t_{in}. This value can then be used to calculate D from equation (3) with little sacrifice of the accuracy of the results. This is because the probing depth of the evanescent wave in the coating films at the water OH stretching band wavelength (2.94 μm) is negligibly small (<$3d_p$ or about 1-2 μm) as compared to the coating thickness. For that reason, the time it takes to detect water within the probing depth of the evanescent wave may be assumed as the same as that for water transported through the entire coating thickness. For all cases of our study, t_{in} values obtained from the intensity-time curve (*Figure* 4) were approximately the same as those obtained from the interfacial water mass-time curve (*Figure* 7). Of course, the thicker the coatings and the higher the refractive index of the substrate, the more accurate the determination of D. Thus, for routine measurement of D of liquid water in thick coatings (> 25 μm) applied to a substrate, the recommended procedure is simply as follows: (1) collecting continuously FTIR-MIR spectra of the coated specimen exposed to water until the increase of the water band intensity levels off (which depends on film thickness and film quality); (2) extrapolating t_{in} from the FTIR-MIR intensity-time curve; (3) measuring the coating thickness; and (4) calculating D from equation (3). Data on water uptake in free films, FTIR-MIR absorbance of water on a coating-free substrate, and penetration depths of the evanescent wave in the coating films and water, which were required to determine $Q_{wi}(t)$ in equations (7) and (9), are not needed.

Among the three internal reflection elements used, Ge and Si were found to be preferred substrates because of their high refractive indices, which allow the detection of water close to the interface (<1 μm in the coatings). If metal is the desired substrate, a thin film (<10 nm for iron) of the metal can be evaporated onto the internal reflection element prior to the coating application.[20] However, care must be exercised when using this organic coating/metal film/substrate configuration, particularly for low-reflective and oxidizable metals. In this case, although water near the coating/metal interface is

Figure 8—Mass-time curve for water at the coating/substrate interface at early exposure stage for determining the time lag, t_{in}. (a) alkyd/SiO$_2$-Si; (b) water-reducible epoxy/Ge; and (c) powder epoxy/KRS-5. (Each dot represents a data point).
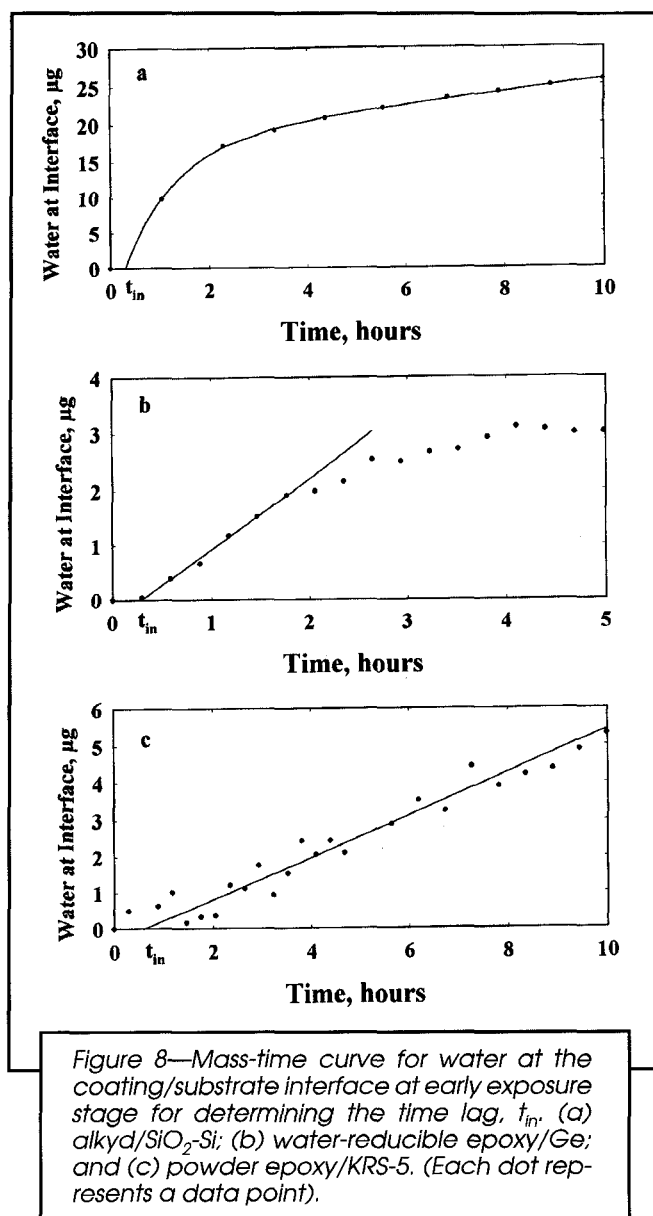
detected, the loss of the metal material due to corrosion during the *in situ* measurement likely complicates the analysis of the FTIR intensity-time curve. Using the method described here, the effects of salt contamination on the substrate surface and the concentration of electrolyte on the water transport through an organic coating applied to a substrate are being investigated. This study will provide information needed to identify the transport processes (osmotic-driven or/and concentration-driven) responsible for blistering and water disbondment of organic protective coatings on metals.

SUMMARY AND CONCLUSIONS

A method based on Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy was developed for measuring the apparent diffusion coefficient of water in a coating applied to a substrate. The method requires an application of a coating, transparent or opaque, of sufficient thickness on an internal reflection element (IRE), which serves as

the substrate. A water chamber is attached to the coated specimen. After adding water to the chamber, FTIR-MIR spectra are collected automatically at specified time intervals without disturbing the specimen or the instrument. Both water at the coating/substrate interface and water in the coating within the probing depth were detected. The amount of water at the coating/substrate interface was determined using a model based on the theory of internal reflection spectroscopy. A mass-time curve for water at the interface was established providing the time-lag value, the time required for water to diffuse through the coating film and reach the interface. The apparent diffusion coefficient (D) is then determined by the time-lag equation. For thick coating films (>25 μm), D may be estimated from the FTIR-MIR *in situ* intensity data only; the laborious task of determining the amount of water at the coating/substrate interface is not required. The sensitivity of FTIR-MIR spectroscopy and the strong FTIR absorption of the water molecules and dissociate groups make this an ideal method for measuring the diffusivity of liquid water through a coating applied to a substrate. This quantity may be used for interpreting corrosion of the substrate, blistering, and water disbondment of organic-coated substrates. Finally, the method should be equally applicable to studies of the transport of water vapor, and organic and inorganic compounds through a coating applied to a substrate.

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